

Dechlorination kinetics of monochlorobiphenyls by Fe/Pd: Effects of solvent, temperature, and PCB concentration

Yuanxiang Fang, Souhail R. Al-Abed *

U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 W. Martin Luther King Dr., Cincinnati, OH 45268, USA

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Abstract

Well-known, yet undefined, changes in the conditions and activity of palladized zerovalent iron (Fe/Pd) over an extended period of time hindered a careful study of dechlorination kinetics in long-term experiments. A short-term experimental method was, therefore, developed to study the effects of temperature and solvent on the dechlorination of monochlorobiphenyls (MCBs), 2-chlorobiphenyl (2-CIBP), in particular by Fe/Pd. The experiments started with specified initial conditions and lasted only for 10 min. The average value (k) of the first-order rate constant for the dechlorination of 2-CIBP was $0.13 \pm 0.03 \text{ L m}^{-2} \text{ h}^{-1}$, not significantly different from the average values for 3-chlorobiphenyl and 4-chlorobiphenyl. The apparent activation energy was $20 \pm 4 \text{ kJ mol}^{-1}$ and $17 \pm 7 \text{ kJ mol}^{-1}$, in a temperature range between 4°C and 60°C , for the dechlorination of 2-CIBP using two batches of Fe/Pd catalyst. The k values decreased significantly in mixtures with a methanol concentration higher than 10%. The values of the rate constant were slightly influenced by the initial concentrations in the experiments at a low temperature and in a solution with a high methanol concentration. The concentration dependence was described with a Langmuir equation, based on the Langmuir–Hinshelwood mechanism that includes an adsorption step of a single species preceding a rate-determining catalytic reaction.

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1. Introduction

Polychlorinated biphenyls (PCBs) are one group of persistent organic pollutants (POPs) that are of international concern because of global distribution, persistence, and toxicity (<http://www.pops.int/>). Removal of these compounds from the environment remains a very difficult challenge because the compounds are highly hydrophobic and have very low solubility in water. They are also recalcitrant to chemical and biological degradations. Current remediation techniques, such as stabilization, dredging, landfill, and solvent extraction are costly; moreover, the contained sediments still require remediation, and the pollutants contained in such extracts need further treatment [1,2]. One cost-effective technology that has the potential to be applied for both in situ and ex situ remediation of PCB contaminations [3–6] is the use of palladized iron [7,8].

Palladized zerovalent iron (Fe/Pd) has been used for effective dechlorination of chlorinated aromatic compounds, such as chlorophenols and chlorobenzenes [9,10], but the dechlorination of PCBs by Fe/Pd has led to results that are quite different. Both complete and incomplete dechlorination has been reported [4,7,8]. The reported rates of dechlorination vary over several orders of magnitude, from $10^{-6} \text{ L m}^{-2} \text{ h}^{-1}$ to $10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ [4,8,11,12]. The catalyst reactivity could be unsustainable [4], and values of the rate constant could decrease over time [12]. The rate of dechlorination was also sensitive to solvents, which are often used for the extraction of PCBs during the remediation of PCB-contaminated soils and sediment [8].

The differences in the reported rates of dechlorination are a result of different, yet unspecified, conditions of the catalysts and reaction conditions that also change during experiments. The catalysts may differ significantly in the sizes of the particles, in Pd loading, and in reactivity that can be further influenced by the buffered or unbuffered reaction media. Both the catalyst and the reaction medium may experience expected,

* Corresponding author. Tel.: +1 513 569 7849; fax: +1 513 569 7879.

E-mail address: al-abad.souhail@epa.gov (S.R. Al-Abed).

yet indefinite, changes during a dechlorination process. Such unspecified variations over time thus make it difficult to study the sensitive effects of the reaction conditions on the dechlorination kinetics in long-term experiments.

In this report, a short-term dechlorination approach was developed to study the kinetics of PCB dechlorination by palladized iron under various conditions. Short-term experiments are often used to obtain the rates of reaction at specified conditions, such as temperature and reactant concentrations [13]. The objective here was to study the effects of temperature and solvent (methanol) on the dechlorination of monochlorobiphenyls (MCBs), especially 2-chlorobiphenyl (one of the most recalcitrant PCB congeners). To our knowledge, the kinetic effects of temperature and solvents have not been systemically investigated. The short-term kinetics were evaluated and compared with the results of dechlorination observed in long-term experiments.

2. Materials and methods

2.1. Chemicals

Iron particles were of the size 210–290 μm obtained from Fisher Scientific. Palladium acetate $(\text{CH}_3\text{CO}_2)_2\text{Pd}$ (purity > 98%) was obtained from GFS Chemicals. Biphenyl (BP) and MCB congeners – 2-ClBP, 3-chlorobiphenyl (3-Cl BP), and 4-chlorobiphenyl (4-Cl BP) – (purity > 99%); the internal standard (3,3',4-trichlorobiphenyl); and standard biphenyl and MCP solutions were obtained from Ultra Scientific. A cosolvent of acetone and hexane (30:70) was prepared for extraction of organic compounds from aqueous solutions and Fe/Pd particles. Hexane (Optima grade) and acetone (GC grade) were from Fisher Scientific. HCl (6N) was from Aldrich. Water used in the experiments was oxygen-free, obtained by bubbling nitrogen gas overnight through Milli-Q water (resistivity $\geq 8 \text{ M}\Omega \text{ cm}$).

2.2. Preparation of Fe/Pd particles

The Fe/Pd particles were prepared using a method that was a modified version of the method used by Zhang et al. [14]. The iron particles were first washed with 6N HCl for 5 s and were then immediately washed five times with oxygen-free Milli-Q water. The acid-washed iron particles were then transferred to a plastic centrifuge tube that had been fully filled with an ethanol solution of $(\text{CH}_3\text{CO}_2)_2\text{Pd}$ (no headspace in the tube). The deposition of palladium lasted for 2 h while the mixture in the tube was mixed on a tumbler mixer. At the end of that time, the ethanol solution was sampled for an analysis for palladium concentration, and the remaining solution was then discarded. The Fe/Pd was washed four times with (oxygen-free) water, each time with the same volume as the ethanol solution (no headspace in the tube).

In this study, four batches of Fe/Pd particles (Batches A–D) were prepared according to the same procedure. All Fe/Pd contained the same Pd loading of 0.585%, which was calculated based on the iron amount (before acid-washing)

and the concentration of $(\text{CH}_3\text{CO}_2)_2\text{Pd}$ in the ethanol solution. This level of Pd loading was used so that a significant fraction of 2-ClBP in a 40 mL solution could be dechlorinated by 0.1 g such Fe/Pd within a few hours.

2.3. Dechlorination of MCBs

The short-term dechlorination of MCBs by freshly prepared Fe/Pd was carried out for 10 min. The time was determined so that only a small fraction (around 10%) of the MCB was dechlorinated at room temperature. In each experiment, there were several sets of 40 mL vials, and each set consisted of five or six vials. A vial set was used for dechlorination under one condition, and the solutions in each set of vials contained different MCB concentrations that ranged between 2 μM and 19 μM . Different vial sets were used for dechlorination under different conditions, including different temperatures or different solvent contents of the solutions. All the vials were fully filled with solutions to prevent any headspace (air); the volumes of the solutions ($43.2 \pm 0.1 \text{ mL}$) were calculated from the weights of the solutions in the vials. About 0.1 g of Fe/Pd was delivered to each vial of a set at a time and that set of vials was immediately placed on a tumbler mixer at 188 rad min^{-1} (30 rpm).

After 10 min, 1.5 mL of solution was taken from each vial in a set and placed into a centrifuge bottle to which a volume of 1.5 mL cosolvent was added (for extraction). The solution could then be (randomly) selected for pH measurement. The rest of the solution was discarded, using a magnetic bar to attract and keep Fe/Pd particles at the bottom of the vial. Then a volume of 4.5 mL cosolvent was added to the vial for the extraction of biphenyls adsorbed on the Fe/Pd particles and on the glass wall.

The same amount of Fe/Pd particles was consistently delivered to each vial in pieces of plastic tubing (of the same length) filled with the Fe/Pd particles. A 3.18 mm i.d. and 6.35 mm, o.d. PTFE tubing was first marked (with a shallow cut) for as many pieces of units as were needed; each piece was 0.4 cm in length. The tubing was then filled with freshly prepared Fe/Pd and was cut in pieces as marked; then the amount of Fe/Pd in one piece was delivered to one vial. All pieces of empty tubing (after being air dried) were weighed, and the actual amount of Fe/Pd in a piece (delivered to one vial) was calculated, based on the weight of the piece, the total weight of all the pieces, and the total amount of Fe particles (before the acid wash).

The long-term dechlorination in various solutions was carried out over a period of 24–216 h. One 40 mL vial was used for each experiment. The experiment started once 0.1 g Fe/Pd was delivered to the vial (using the same method as in short-term experiments). The suspension was tumbler-mixed at 188 rad min^{-1} (30 rpm) during the experiment. At each sampling time, a 1 mL solution was taken from the solution under a nitrogen environment (O_2 -free) and extracted with 2 mL of cosolvent in a centrifuge bottle. At the end, the solution was discarded and the Fe/Pd particles were extracted using a 4.5 mL of cosolvent.

2.4. Analytical methods

The sample vials and bottles were placed in a shaker for the extraction of biphenyls; the extraction was carried out for 18 h at 35 °C. The top extracts (0.5 mL) were then transferred to 2-μL GC vials from the extraction bottles and vials after the bottles were centrifuged at 1350 rpm for 10 min and the particles in the vials allowed to settle for 2 h. After being injected with a 10 μL internal standard, the extracts were analyzed using the HP 5980 GC/MS based on the EPA SW-846 method 8270C for semi-volatile organic compounds such as PCBs (http://www.epa.gov/epaoswer/hazwaste/test/8_series.html). The GC/MS was equipped with a Supelco SPB-5 30 m × 0.32 μm × 0.25 μm column. Calibration curves were developed based on six-point data with coefficients of determination (r^2) greater than 0.998; the detection limit for the method was 50 μg L⁻¹ for the biphenyls. The efficiency of extraction of the biphenyls on Fe/Pd and in the solution was 85–95%. The palladium samples were analyzed using an IRIS Intrepid ICP spectrometer (Thermo Elemental). The detection limit was 0.5 mg L⁻¹.

3. Results and discussion

3.1. Dechlorination of 2-CIBP by Fe/Pd

The palladium in the ethanol solution was completely deposited on the iron particles in 2 h, because the Pd

concentration in the final solutions was below the detection limit. The actual Pd loading could vary slightly from batch to batch because a small amount of fine iron particles and Fe/Pd particles were lost (but not quantified) during acid washing and the post-deposition water washing. The amount of Fe/Pd delivered to each vial in the experiments was very consistent, averaging about 0.100 g of Fe with an average standard deviation of less than 0.005 g and based on more than 40 Fe/Pd samples. The initial 2-CIBP solutions were pH 8.3. The pH values were 8.48, 8.44, 8.46, 8.33, and 8.08 in the solutions that initially contained 2 μM, 4 μM, 8 μM, 12 μM, and 16 μM 2-CIBP at the end of a short-term experiment (listed in Table 1) that used the Fe/Pd from Batch A. In a duplicate experiment (also listed in Table 1) that used the Fe/Pd from the same batch, the final pH values in the solutions that initially contained 2 μM and 16 μM 2-CIBP were 8.84 and 8.64, respectively. These measurements indicate some small variations in the final pH values of the solutions that initially contained different 2-CIBP concentrations.

Table 1 summarizes the results of three short-term experiments using the Fe/Pd from Batches A and B. The values in each column were calculated using a formula provided in Table SI 1 [15]. In these short-term experiments, between 10% and 12% of 2-CIBP (based on initial amounts of 2-CIBP) was dechlorinated to biphenyl within 10 min. At the end, about 9–12% of biphenyls was adsorbed on the Fe/Pd, of which about 14–24% was 2-CIBP. Between 87% and 100% of 2-CIBP in the initial solutions were recovered in the form of biphenyl and 2-CIBP.

Table 1
Short-term and long-term dechlorination of 2-CIBP by Fe/Pd^a

C_0 (μM) ^b	Recovery (%)	Conversion (%)	Biphenyls on Fe/Pd (%)	2-CIBP on Fe/Pd (%)	First-order rate constant (L g ⁻¹ h ⁻¹) ^c k (R_{BP}^2 , R_{IBP}^2 , N) ^d	Fe/Pd batch
Short-term ^d						
2–19	100 ± 3	12 ± 1	12 ± 1	22 ± 5	0.29 ± 0.03 (0.992, 0.998, 5)	A
2–19	93 ± 3	11 ± 1	11 ± 1	24 ± 2	0.28 ± 0.03 (0.984, 0.999, 5)	A
2–17	87 ± 3	10 ± 1	9 ± 1	14 ± 5	0.28 ± 0.02 (0.998, 0.997, 5)	B
C_0 (μM)	Recovery (%)	Conversion (%)	Biphenyls on Fe/Pd (%)	2-CIBP on Fe/Pd (%)	First-order rate constant (L g ⁻¹ h ⁻¹) k_{obs} (R^2 , N) ^e k_{actual} (R^2 , N) ^e	Fe/Pd batch
Long-term ^e						
8.5	89	88.9	45	1	0.50 ± 0.23 (0.977, 4) N/A	A
18.6	89	88.9	33	0	0.50 ± 0.26 (0.971, 4) N/A	A
12	75 ± 2	45–74 ^f	38 ± 4 ^f	7 ± 7 ^f	0.20 ± 0.08 (0.890, 6) 0.17 ± 0.22 (0.849, 4)	B
16	78 ± 2	47–78 ^f	30 ± 2 ^f	4 ± 2 ^f	0.20 ± 0.04 (0.964, 7) 0.18 ± 0.11 (0.960, 4)	B

^a All the experiments were conducted in oxygen-free Milli-Q water at room temperature (23.3 °C) using 0.1 g Fe/Pd with a Pd loading of 0.585%. The formula used to calculate column values are provided in Table SI 1 for short-term dechlorination and in SI 2 for long-term dechlorination [15]. For the short-term experiments, the average (and standard deviation) of values of a variable (columns except for the rate constants) calculated for each of the five vials in a set is listed. The recovery of biphenyls (BP and 2-CIBP) is the percentage of the final total amount of biphenyls over the initial amount of 2-CIBP in a vial. The conversion is the percentage of the final biphenyl amount over the initial amount of 2-CIBP in a vial. The amount of biphenyls on Fe/Pd is the percentage of biphenyls extracted from the Fe/Pd particles among the total biphenyls. The 2-CIBP on Fe/Pd is the percentage of 2-CIBP among the biphenyls extracted from the Fe/Pd.

^b The initial concentration or a range of initial concentration for each experiment.

^c 95% confidence interval was provided for all the values of first-order rate constant; R^2 is the linearity of the data fitting; N is the number of data points.

^d Short-term dechlorination was carried out for 10 min in solutions with a range of initial concentrations as listed. The results from one experiment with Fe/Pd from Batch B are presented in Fig. 1a. As shown in Fig. 1a, R_{BP}^2 is the linearity of the biphenyl amounts vs. the initial 2-CIBP amounts and R_{IBP}^2 is the linearity of the amounts of total biphenyls vs. the initial 2-CIBP amounts.

^e All the data were obtained at the end of the experiments, except for the rate constant values and the ranges of conversion values in samples from the sacrificed vials. The k_{obs} values were calculated from the exponential decrease of the 2-CIBP amount in the aqueous phase. The k_{actual} values were calculated based on the exponential decrease of the total 2-CIBP amount in the vials.

^f The values were the averages of the samples from six sacrificed vials.

Because 2-CIBP and biphenyl (the product) distribute both in the solution and on the Fe/Pd, the rate of short-term dechlorination of 2-CIBP that follows first-order kinetics is expressed in Eq. (1). The first-order rate constant k is defined in Eq. (2).

$$-V_R \left(\frac{dC_{2\text{-CIBP}}}{dt} \right)_{\text{dechlorination}} = kWC_{2\text{-CIBP}} \equiv V_R \frac{dC_{BP}}{dt} + W \frac{dG_{BP}}{dt} \quad (1)$$

$$k \equiv \frac{V_R(dC_{BP}/dt) + W(dG_{BP}/dt)}{WC_{2\text{-CIBP}}} \quad (2)$$

In Eqs. (1) and (2), C (μM) is the concentration of biphenyl or 2-CIBP in the solution; G ($\mu\text{mol g}^{-1}$) the concentration of biphenyl or 2-CIBP on the Fe/Pd (based on the weight of the catalyst); t (h) the time; V_R (L) the volume of solution; and W (g) is the amount of Fe/Pd.

Because the initial G and C values for biphenyl were zero, a value of k can be calculated using Eq. (3) based on the final amounts of biphenyl and 2-CIBP obtained in each vial.

$$k = \frac{V_R C_{BP} + W G_{BP}}{V_R(C_{2\text{-CIBP}} + C_{BP}) + W(G_{2\text{-CIBP}} + G_{BP})} \frac{V_R}{W t_R} = \frac{m_{BP}}{m_{2\text{-CIBP}} + m_{BP}} \frac{V_R}{W t_R} \quad (3)$$

where m (μmol) is the final total amount of biphenyl or 2-CIBP in the vial; and t_R (h) is the experiment time (10 min).

For an experiment that includes a set of vials, each vial contains a solution of different (initial) 2-CIBP concentration; an average of k can be obtained from the individual k values for the dechlorination of 2-CIBP over the covered concentration range. However, such an average carries a relatively large variation, because the k value for a vial with an initial solution of a lower concentration carries a relatively greater uncertainty due to a smaller value (of the initial 2-CIBP amount) in the denominator. Therefore, Eq. (2) was transformed to calculate

an average value of k with a smaller deviation by directly using all the primary data obtained from all the vials in a set.

The values of k , being a first-order rate constant, should theoretically be independent of $C_{2\text{-CIBP},0}$ (the initial concentration of 2-CIBP) and of the ratio (in Eq. (3)) of m_{BP} to $(m_{BP} + m_{2\text{-CIBP}})$. Such independence was observed in the short-term experiments presented in Table 1 and is illustrated in Fig. 1a for the experiment using Fe/Pd from Batch B. Fig. 1a plots m_{BP} and $m_{BP} + m_{2\text{-CIBP}}$ (m_{tBP}) versus the initial amounts of 2-CIBP ($m_{tBP,0}$) for the experiment. The values of $m_{tBP,0}$, calculated from the dilution ratios used in the preparation of the vials, are different from the m_{tBP} values due to experimental and analytical uncertainties. Fig. 1a also demonstrates that the slope of the m_{BP} line (through the origin) is independent of the $m_{2\text{-CIBP},0}$ values, such independence results in the establishment of Eq. (4), which leads to Eqs. (3)–(5):

$$\begin{aligned} & \left(\frac{m_{BP}/m_{2\text{-CIBP},0}}{(m_{2\text{-CIBP}} + m_{BP})/m_{2\text{-CIBP},0}} \right)_1 \\ &= \left(\frac{m_{BP}/m_{2\text{-CIBP},0}}{(m_{2\text{-CIBP}} + m_{BP})/m_{2\text{-CIBP},0}} \right)_2 = \dots \\ &= \left(\frac{m_{BP}/m_{2\text{-CIBP},0}}{(m_{2\text{-CIBP}} + m_{BP})/m_{2\text{-CIBP},0}} \right)_i = \dots = \frac{q_{BP}}{q_{tBP}} \quad (4) \end{aligned}$$

$$\underline{k} = \frac{q_{BP}}{q_{tBP}} \frac{\bar{V}_R}{\bar{W} t_R} \quad (5)$$

where \underline{k} ($\text{L g}^{-1} \text{h}^{-1}$) is an average value of the rate constant for the short-term dechlorination in the vials of the set. In Eqs. (4) and (5), $i = 1, 2, \dots$ designates different vials in the set; q_{BP} and q_{tBP} are the slopes of the lines of m_{BP} and m_{tBP} over $m_{tBP,0}$, respectively; \bar{V}_R (L) and \bar{W} (g) are the average volume and the Fe/Pd amount in the vials. The \underline{k} value carries a smaller variation than the average of the individual k values calculated using Eq. (3), because the q_{BP} and q_{tBP} values carry smaller uncertainties than do the individual values of m_{BP} and m_{tBP} . The variation of the \underline{k} value can be represented by the 95% of

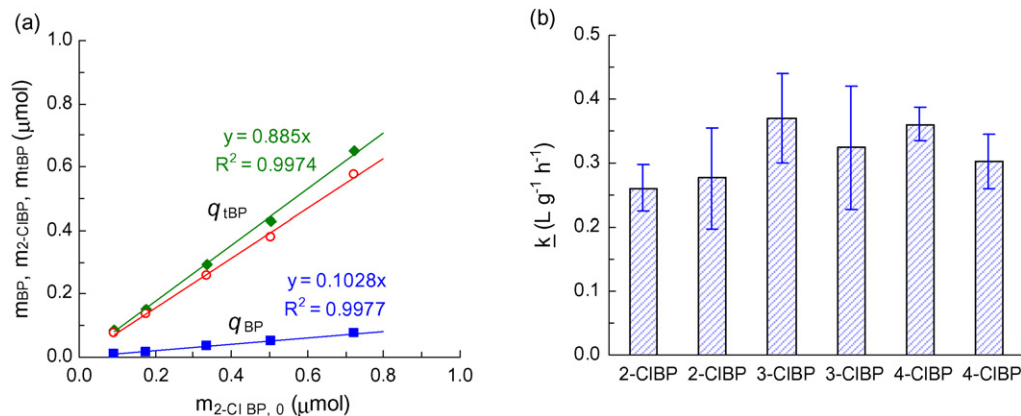


Fig. 1. (a) The amounts of biphenyl (\blacksquare , m_{BP}), 2-CIBP (\bullet , $m_{2\text{-CIBP}}$), and total biphenyls (\blacklozenge , m_{tBP}) after 10 min dechlorination of 2-CIBP by Fe/Pd (from Batch B) vs. the initial amounts of 2-CIBP ($m_{2\text{-CIBP},0}$) in a set of short-term experiment (listed in Table 1), q_{tBP} is the slope of m_{tBP} vs. $m_{2\text{-CIBP},0}$, and q_{BP} is the slope of m_{BP} vs. $m_{2\text{-CIBP},0}$; (b) the values of first-order rate constants \underline{k} and their 95% confidence intervals for the dechlorination of 2-, 3-, and 4-CIBP in water using Fe/Pd from one single batch (not listed in Table 1).

confidence interval ($\pm k$), which can be estimated using the following equation,

$$\pm k = \frac{\bar{V}_R}{\bar{W}t_R} \frac{\pm q_{BP}q_{IBP} + q_{BP}(\pm q_{IBP})}{q_{IBP}^2} \quad (6)$$

where $\pm q_{BP}$ and $\pm q_{IBP}$ are the 95% confidence intervals of q_{BP} and q_{IBP} , respectively, and their values are estimated using $t_v S_b$, where t_v is the critical value of the t statistic and S_b is the standard error in the slope.

The k values for the three, short-term experiments, listed in Table 1, are $0.28 \text{ L g}^{-1} \text{ h}^{-1}$ and $0.29 \text{ L g}^{-1} \text{ h}^{-1}$ with a very small 95% confidence interval of $0.03 \text{ L g}^{-1} \text{ h}^{-1}$. The surface area normalized rate constant value is about $0.13 \pm 0.03 \text{ L m}^{-2} \text{ h}^{-1}$, calculated based on an average specific surface area (N_2 -BET) of $2.21 \text{ m}^2 \text{ g}^{-1}$ (with a relative percentage difference of 0.2%) for one batch of Fe/Pd particles (after water-washing and drying in N_2). The rate constant values are of the same magnitude as those for the dechlorination of monochlorophenols and *p*-dichlorobenzene [9,10] and the dechlorination of PCBs [8,12]. In particular, the k values for short-term dechlorination are more consistent and carry smaller 95% confidence intervals than do the rate constant values observed in the following long-term experiments.

In the two, long-term experiments using Batch A Fe/Pd (the results of which are summarized in Table 1), 2-CIBP was completely removed from the solutions within the first 4 h (data are not presented). The apparent first-order rate constant k_{obs} , calculated using all the non-zero concentration data (four points) obtained in the first 4 h, was $0.50 \text{ L g}^{-1} \text{ h}^{-1}$ with relatively large 95% confidence intervals due to limited, non-zero data points. About 33% and 45% of total biphenyls, respectively, were found adsorbed on Fe/Pd at the end of experiments (which lasted for 216 h); among the adsorbed, more than 99% were biphenyl. Because significant amounts of 2-CIBP and biphenyl remained adsorbed on the Fe/Pd particles, the k_{obs} values that were based on the changes of 2-CIBP concentration (or amount) in the aqueous phase tended to be overestimated.

To evaluate the extent of overestimation of the k_{obs} values, long-term experiments were conducted with vials that were sacrificed during the experiments to obtain the total amounts of biphenyl and 2-CIBP in the vials. For each experiment, several vials were used with solutions that initially contained the same concentrations of 2-CIBP. At one of a few sampling times, one vial was sacrificed; a sample of 1.5 mL solution was taken and extracted with 1.5 mL cosolvent, and the Fe/Pd particles were extracted with a 4.5 mL of cosolvent. Table 1 summarizes the results of two of such long-term experiments that used Fe/Pd from Batch B. Based on the samples from four sacrificed vials, about 38% and 30% of total biphenyls was adsorbed on the Fe/Pd particles, of which about 7% and 4% was 2-CIBP. For the experiment that started with an initial concentration of $16 \mu\text{M}$, Fig. 2 shows the temporal profiles of the amounts of 2-CIBP in the aqueous phase and the total amounts of 2-CIBP in the vials. For these two experiments, the values of the actual rate constant (k_{actual}), calculated based on the exponential decrease of the

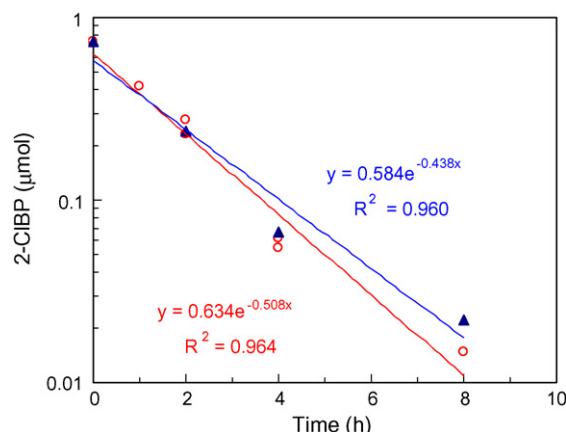


Fig. 2. Exponential decreases of the amounts of 2-CIBP in the aqueous phase (○) and in the entire reactor vials (▲) during the first 8-h in the long-term experiments of dechlorination using Fe/Pd from Batch B.

total amounts of 2-CIBP in the vials, were $0.17 \text{ L m}^{-2} \text{ h}^{-1}$ and $0.18 \text{ L m}^{-2} \text{ h}^{-1}$, the 95% confidence intervals are relatively large because of the small number of samples from the sacrificed vials. These k_{actual} values are about 16% smaller than the k_{obs} values which were calculated based on the exponential decrease of the 2-CIBP amount in the solutions. However, for such a difference to be statistically significant, values of k_{actual} with a much smaller variation are needed from experiments with more samples from the sacrificed vials.

The k_{obs} value for the experiment that started with the initial concentration of $16 \mu\text{M}$, which should be bigger than the actual rate constant, is nevertheless (statistically) significantly smaller than the k values in the short-term experiments, suggesting a low catalytic activity of Fe/Pd in the long-term experiments. (For other long-term experiments, the differences between the values of k_{actual} or k_{obs} and the k values were not statistically significant due to the large variations in the rate constant values from the long-term experiments.) The activity decrease was a result of iron corrosion which had caused the precipitation of iron oxides (passivation) at the Fe/Pd surface and the covering of the active sites, and thus reduced the catalyst's reactivity [4,12].

The solution pH was not monitored in the long-term experiments, but the final pH was higher than the initial value, as observed in the short-term experiments. Iron corrosion in solutions of pH higher than 7 tends to form a passive film of iron oxides and hydroxide on the iron surface [16], which increases the resistance to the transfer of electrons cross the film and thus inhibits further decomposition of the iron. As a result, the catalyst activity decreases. These effects were not significantly manifested in the results of the short-term experiments because the time of the experiments was short, the Fe/Pd catalysts were freshly prepared, and the initial pH of the solutions was the same.

3.2. Dechlorination of MCBs by Fe/Pd

The dechlorination experiments of three monochlorobiphenyls were conducted using Fe/Pd from a single batch (not listed

in Table 1); the values of k and their 95% confidence intervals are plotted in Fig. 1b. These values indicate that 2-CIBP was dechlorinated at a rate not statistically different from 3-CIBP and 4-CIBP; the *meta*- and *ortho*-substituted isomers were dechlorinated at rates not significantly different. The clear and complete order (4-CIBP > 3-CIBP > 2-CIBP) in the rates of dechlorination of three MCBs observed by Kim et al. was not observed here [11].

The amounts of total biphenyls adsorbed on Fe/Pd in the dechlorination 3-CIBP and 4-CIBP were almost double the amount of total biphenyls on Fe/Pd. Among those adsorbed biphenyls, the percentages of 3-CIBP and 4-CIBP were almost triple the percentage of 2-CIBP (data not presented). The results are consistent with and can be reasonably explained by their values of $\log K_{ow}$ (4.58, 4.71, 4.74, respectively for 2-, 3-, 4-CIBP) [17]. Compounds of higher hydrophobicity tend to be adsorbed more abundantly.

3.3. Temperature effect

Table 2 summarizes the results of short-term dechlorination of 2-CIBP at different temperatures using the Fe/Pd from Batches C and D. At a higher temperature, more of the total biphenyls were adsorbed by Fe/Pd, but the percentages of 2-CIBP among the adsorbed biphenyls were lower because the dechlorination occurred faster at a higher temperature. At a given temperature, the dechlorination of 2-CIBP in a set of vials was conducted, and a k value was calculated. The k value increases as the temperature increases. The apparent activation energy E_a was 20 ± 4 kJ/mol between 4 °C and 60 °C and

17 ± 7 kJ/mol between 4 °C and 51 °C for the dechlorination, using the Fe/Pd from Batches C and D, respectively. The low E_a values (in the range of the heat of adsorption), which may include temperature effects on other processes such as sorption, are the result of the Pd catalyst that reduced the dechlorination activation energy [14].

3.4. Effect of initial concentration

The values of k are slightly related to the initial concentration of 2-CIBP, and the weak relation is demonstrated in Fig. 3, which plots the reciprocal of k versus the initial concentration of 2-CIBP for the dechlorination of 2-CIBP under several temperatures using the Fe/Pd from Batch C. The relationship presented in Fig. 3 can be described by Eqs. (7) and (8), which describe the reactions of a single species on a simple catalyst surface following a Langmuir–Hinshelwood mechanism [18],

$$r_{2\text{-CIBP}} \equiv \left(-\frac{dC_{2\text{-CIBP}}}{dt} \right) \frac{V_R}{W} = \frac{k_A C_{2\text{-CIBP}}}{1 + (C_{2\text{-CIBP}}/K_A)} \quad (7)$$

$$\frac{C_{2\text{-CIBP}}}{r_{2\text{-CIBP}}} \equiv \frac{1}{k} = \frac{1}{k_A} + \frac{1}{k_A} \frac{C_{2\text{-CIBP}}}{K_A} = b + qC_{2\text{-CIBP}} \quad (8)$$

where K_A (μM) is the reciprocal of the equilibrium constant for the adsorption of 2-CIBP on the reactive sites: 2-CIBP (in solution) + reactive sites \leftrightarrow 2-CIBP (adsorbed); k_A ($\text{L g}^{-1} \text{h}^{-1}$) is a rate constant, which should be k_0/K_A (k_0 is a zero-order rate constant) in a standard Langmuir rate equation, and used here to compare its values with the values of k (as $C_{2\text{-CIBP}}$ approaches

Table 2
Dechlorination of 2-CIBP by Fe/Pd at different temperatures^a

T (°C)	Recovery (%)	Conversion (%)	Biphenyl on Fe/Pd (%)	2-CIBP on Fe/Pd (%)	\underline{k} (L g ⁻¹ h ⁻¹)	k_A (L g ⁻¹ h ⁻¹) ^b	K_A (μM) ^b
Fe/Pd from Batch C							
4.0	106 ± 14	10 ± 3	8 ± 1	21 ± 1	0.23 ± 0.03	0.34 ± 0.04	22 ± 3
	103 ± 13	10 ± 2	8 ± 1	21 ± 1	0.23 ± 0.04		
23.3	109 ± 13	16 ± 3	11 ± 2	15 ± 2	0.35 ± 0.04	0.47 ± 0.06	27 ± 6
	106 ± 14	16 ± 4	11 ± 1	17 ± 2	0.36 ± 0.07		
36.5 ^c	97 ± 11	20 ± 4	14 ± 2	18 ± 3	0.47 ± 0.09	0.68 ± 0.07	25 ± 4
60.0	94 ± 13	40 ± 6	16 ± 2	8 ± 1	1.09 ± 0.13	1.17 ± 0.08	75 ± 38
	97 ± 15	39 ± 9	15 ± 4	9 ± 2	0.92 ± 0.21		
Fe/Pd from Batch D							
4.0	95 ± 8	8 ± 1	8 ± 1	26 ± 2	0.19 ± 0.06	0.27 ± 0.04	32 ± 11
23.3	95 ± 7	13 ± 3	11 ± 3	15 ± 2	0.30 ± 0.06	0.44 ± 0.32	25 ± 28
36.5	82 ± 2	17 ± 4	15 ± 2	14 ± 3	0.46 ± 0.07	0.69 ± 0.21	27 ± 15
51.0	93 ± 5	20 ± 1	13 ± 1	7 ± 1	0.56 ± 0.04	0.68 ± 0.12	61 ± 50

^a All the experiments were conducted in oxygen-free Milli-Q water using 0.1 g Fe/Pd with a Pd loading of 0.585%. The formula used to calculate column values are provided in Table SI 1 [15]. The initial concentrations in the five vials of each set were between 2 μM and 16 μM . The average (and standard deviation) of values of a variable (columns except for k , k_A , and K_A) calculated for each of the five vials in a set is listed. The recovery of biphenyls (BP and 2-CIBP) is the percentage of the final total amount of biphenyls over the initial amount of 2-CIBP in a vial. The conversion is the percentage of the final biphenyl amount over the initial amount of 2-CIBP in a vial. The amount of biphenyls on Fe/Pd is the percentage of biphenyls extracted from the Fe/Pd particles among the total biphenyls. The 2-CIBP on Fe/Pd is the percentage of 2-CIBP among the biphenyls extracted from the Fe/Pd. Values and their 95% confidence intervals are listed for k , k_A and K_A .

^b Values of k_A and K_A were calculated by fitting Eq. (8) to experimental data. Data from two duplicate runs at a given temperature were combined and used for the fitting so that deviations in the parameter values could be minimized.

^c Data from one of the duplicates at 36.5 °C were not used because these data deviated from the rest of the data due to unidentified experimental errors.

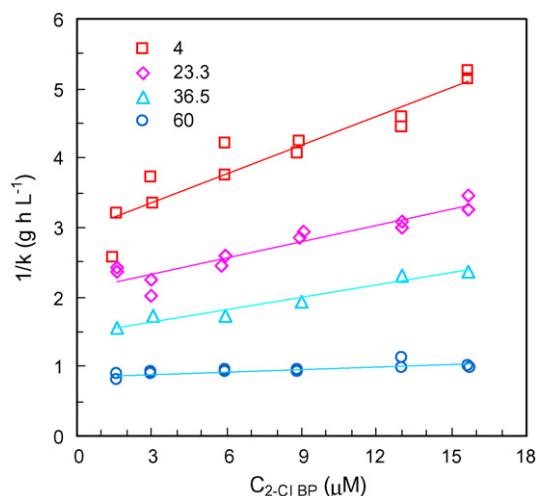


Fig. 3. Dependence of the individual values of the rate constant k (plotted in its reciprocal) on the initial concentrations in the experiments of 2-CIBP dechlorination using Batch C Fe/Pd at different temperatures (numbers in °C).

zero); $r_{2\text{-CIBP}}$ ($\text{mol g}^{-1} \text{h}^{-1}$) is the reaction rate of 2-CIBP at $C_{2\text{-CIBP}}$. In Eq. (8), b ($\equiv 1/k_A$) is the intercept of the line of $1/k$ versus $C_{2\text{-CIBP}}$ at $C_{2\text{-CIBP}} = 0$, and q ($\equiv 1/k_A K_A$) is the slope of the line of $1/k$ versus $C_{2\text{-CIBP}}$. This mechanism assumes that 2-CIBP is first adsorbed on the (reactive) surface sites according to the Langmuir adsorption isotherm and is then dechlorinated at the sites (the rate-determining step) to biphenyl. The values of k_A and K_A can be identified by fitting Eq. (8) to the data of $C_{2\text{-CIBP}}/r_{2\text{-CIBP}}$ ($\equiv 1/k$) plotted against $C_{2\text{-CIBP}}$ as shown in Fig. 3. For an experiment with a set of vials (conducted at a given temperature), $k_A = 1/b$ and $K_A = b/q$. It should be noted that the

K_A value could be different from the saturation concentration of the Langmuir isotherm for the adsorption of 2-CIBP on Fe/Pd particles, which possess both adsorptive and reactive sites.

Table 2 lists the values of k_A and K_A (and their respective 95% confidence intervals $\pm k_A$ and $\pm K_A$) for the dechlorination of 2-CIBP at several temperatures by Fe/Pd from Batches C and D. The values of $\pm k_A$ were estimated from $\pm b/b^2$, where $\pm b$ is the 95% confidence intervals of the b values (estimated using $t_v S_b$, where t_v is the critical value of the t statistic and S_b is the standard error of the intercept). The values of $\pm K_A$ were estimated from $[\pm bq + b(\pm q)]/q^2$, where $\pm q$ is the 95% confidence intervals of the q values (estimated using $t_v S_b$, where t_v is the critical value of the t statistic and S_b is the standard error of the slope). The k_A values are greater than the k values at a given temperature, and the k_A value increases as the temperature increases. The apparent activation energy is $17 \pm 8 \text{ kJ/mol}$ and $16 \pm 14 \text{ kJ/mol}$ for the dechlorination, using Fe/Pd from Batches C and D, respectively. The K_A values, with a relatively large 95% confidence interval though, however, are $61 \mu\text{M}$ and $75 \mu\text{M}$, respectively, at temperatures of 51°C and 60°C , which are bigger than the K_A values at lower temperatures.

Concentration dependence has been observed in the microbial dechlorination and gamma radiolysis of PCBs [19–21], but has not been reported in the dechlorination of chlorinated organics using Fe/Pd. Such dependence has been related to the adsorption (or desorption), a hypothesis that is supported in part by the low apparent activation energy close to the heat of adsorption [22]. Indeed, the dependence may be a manifestation of the adsorption equilibrium in an overall process that proceeds at a slow rate. In a slow process, such as

Table 3
Dechlorination of 2-CIBP by Fe/Pd in methanol–water mixtures^a

Methanol content (%)	Recovery (%)	Conversion (%)	Biphenyls on Fe/Pd (%)	2-CIBP on Fe/Pd (%)	Rate constant ($\text{L g}^{-1} \text{h}^{-1}$), \underline{k}	k_A ($\text{L g}^{-1} \text{h}^{-1}$)	K_A (μM)	Comments (N)
Short-term ^b								
0	87 ± 3	10.0 ± 0.6	8.8 ± 0.5	13.6 ± 4.8	0.30 ± 0.02	N/A ^c	N/A ^c	6
5	80 ± 3	9.7 ± 0.6	7.9 ± 0.8	0.3 ± 0.1	0.30 ± 0.03	0.41 ± 0.07	26.6 ± 7.4	6
10	77 ± 2	8.9 ± 0.8	7.6 ± 0.4	0.3 ± 0.1	0.29 ± 0.03	0.29 ± 0.03	81.2 ± 51.6	6
20	78 ± 2	7.7 ± 0.2	6.7 ± 0.3	0.4 ± 0.1	0.24 ± 0.07	0.31 ± 0.16	25.1 ± 29.7	4
30	75 ± 3	6.5 ± 0.4	5.5 ± 0.6	0.3 ± 0.1	0.21 ± 0.04	0.24 ± 0.03	38.4 ± 18.7	4
Methanol content (%)	Recovery (%)	Conversion (%)	Biphenyls on Fe/Pd (%)	2-CIBP on Fe/Pd (%)	Rate constant ($\text{L g}^{-1} \text{h}^{-1}$), k_{obs}	k_A ($\text{L g}^{-1} \text{h}^{-1}$)	K_A (μM)	C_0 (μM), $R^2(N)$
Long-term ^d								
10	90	85	28	0	0.14 ± 0.07	N/A	N/A	27.3, 0.999 (3)
20	91	85	23	0	0.07 ± 0.05	N/A	N/A	20.6, 0.991 (4)
30	100	88	14	0	0.03 ± 0.01	N/A	N/A	24.7, 0.947 (5)

^a All the experiments were conducted at room temperature (23.3°C) using 0.1 g Fe/Pd with a Pd loading of 0.585% . The formula used to calculate column values are provided in Table SI 1 for short-term dechlorination and in SI 2 for long-term dechlorination [15]. For the short-term experiment, the average (and standard deviation) of values of a variable (columns except for k , k_A , and K_A) calculated for each of the five vials in a set is listed. The recovery of biphenyls (BP and 2-CIBP) is the percentage of the final total amount of biphenyls over the initial amount of 2-CIBP in a vial. The conversion is the percentage of the final biphenyl amount over the initial amount of 2-CIBP in a vial. The amount of biphenyls on Fe/Pd is the percentage of biphenyls extracted from the Fe/Pd particles among the total biphenyls. The 2-CIBP on Fe/Pd is the percentage of 2-CIBP among the biphenyls extracted from the Fe/Pd. Values and their 95% confidence intervals are listed for \underline{k} , k_A and K_A . The number of data points (N) used for the fitting are also listed.

^b Short-term dechlorination was carried out for 10 min using Fe/Pd from Batch B; the initial concentrations of 2-CIBP were between $2 \mu\text{M}$ and $16 \mu\text{M}$.

^c Data are not available because the line, shown in Fig. 4b, of $1/k$ vs. $C_{2\text{-CIBP}}$ is horizontal.

^d Long-term dechlorination was carried out for 2 weeks using Fe/Pd from Batch D. The k_{obs} values were calculated based on the exponential decrease of non-zero concentration data over time. C_0 is the initial concentration of 2-CIBP. R^2 is the linearity of the fitting, and N is the number of data points used.

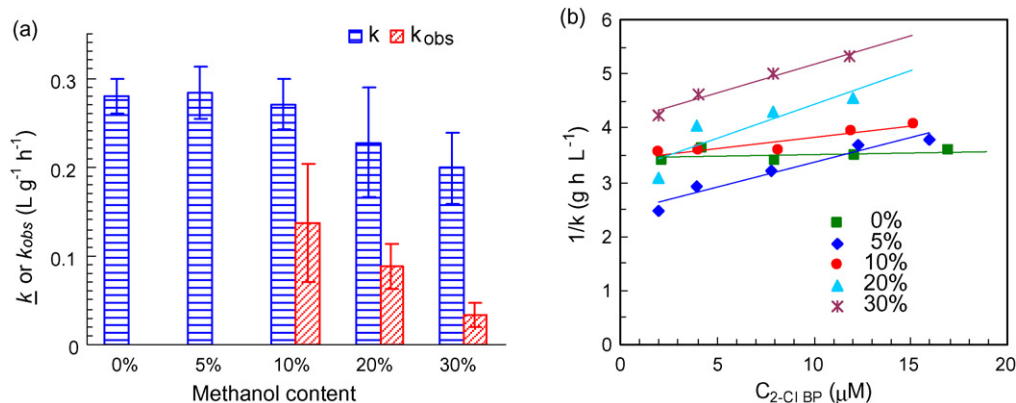


Fig. 4. (a) The values of k and k_{obs} for the short-term and long-term dechlorination of 2-CIBP in mixtures with different methanol contents; (b) the influence of methanol contents on the weak dependence of the k values on 2-CIBP concentrations.

the microbial dechlorination of PCBs, the impact of the equilibrium of adsorption (and desorption) becomes more distinct. And the values of the observed first-order rate constant tend to vary with the PCB concentration. In a faster process of dechlorination such as using highly reactive Fe/Pd or Fe/Pd nanoparticles, PCBs can be dechlorinated on the catalyst surface at a rate closer to (but still less than) the rate of adsorption. In such a process, equilibrium of adsorption is not fully attained because the adsorbed molecules are quickly dechlorinated. As a result, the impact of adsorption equilibrium is not significant, and the concentration dependence on the apparent rate constant is not observable. (When the reaction rate is equal to or faster than the adsorption rate, the reactant molecules are dechlorinated once they reach the reactive sites and adsorption equilibrium is not attained. In that case, the overall rate is limited by the adsorption, and the apparent rate constant is independent of the concentration.) This explanation is consistent with the evidence that some of the 2-CIBP molecules remained adsorbed on the Fe/Pd catalyst and that the concentration dependence was more remarkable at lower temperatures when the dechlorination rate was slower.

3.5. Effects of methanol (solvent)

The results presented in Table 3 and Fig. 4 for the short-term dechlorination of 2-CIBP at 23 °C indicate that the presence of methanol resulted in a lesser amount of total biphenyls being adsorbed on the Fe/Pd particles and a slower rate of dechlorination. The k values, shown in Fig. 4a, were significantly lower in solutions that had a methanol concentration higher than 10%. The concentration dependence of the rate constant k , demonstrated in Fig. 4b, became more remarkable in solutions that contained higher methanol concentration. In Fig. 4b, only four data points were presented for experiments in solutions with 20% and 30% methanol, because these initial solutions were prepared (incorrectly) by injection of a 2-CIBP stock (in methanol) and the initial concentrations were much lower than the expected values. All the other initial solutions were prepared by diluting an aqueous stock solution (with a 2-CIBP concentration that was close to saturation).

For long-term dechlorination, Fig. 5 shows temporal profiles of biphenyl and 2-CIBP in the solutions that contained different methanol contents. The k_{obs} values, calculated based on the exponential decrease of the 2-CIBP concentration over time, become smaller in solutions that contained a higher concentration of methanol. The decrease in the k_{obs} values was consistent with the slow increase of biphenyl in solutions that contained a higher concentration of methanol. In solutions with the same methanol content, the k_{obs} values in the long-term experiments were smaller than the k values for the short-term dechlorination, as shown in Fig. 4a. The difference increases as the methanol concentration increases. Note that the Fe/Pd particles used in the short-term and long-term experiments came, respectively, from Batches B and D; nevertheless, the k values for the short-term dechlorination of 2-CIBP, using these two batches of Fe/Pd, are statistically the same (data presented, respectively, in Tables 2 and 1). The final biphenyl concentration in Fig. 5 is lower in the 20% methanol solution than in the 10% methanol solution because the initial 2-CIBP concentration in the 20% methanol solution was lower. The values of 2-CIBP conversion in the long-term experiments (listed in Table 3) were smaller

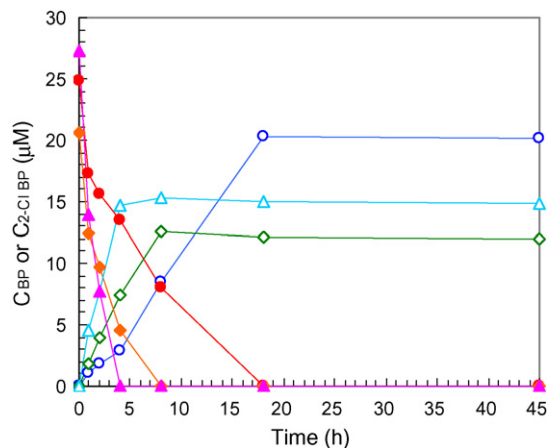


Fig. 5. Temporal profiles of 2-CIBP (filled symbols) and biphenyl (open symbols) in the long-term experiment of 2-CIBP dechlorination in mixtures that contained (\triangle , \blacktriangle) 10%, (\diamond , \blacklozenge) 20%, and (\circ , \bullet) 30% methanol.

than the recovery values because the amount of 2-CIBP in the samples (that were taken out during the experiments) had not been converted to biphenyl.

These methanol effects can be related to their influence on the solubility of the biphenyls and the redox potential of the methanol solutions. The addition of methanol enhances the solubility of biphenyl and 2-CIBP, shifting the adsorption equilibrium and reducing the amounts of biphenyl and 2-CIBP adsorbed on the Fe/Pd particles. The addition of methanol also lowers the redox potential of the mixtures: the redox potentials measured in the mixtures that contained 0%, 5%, 10%, 20%, and 30% methanol were 121 mV, 80 mV, 68 mV, 56 mV, and 36 mV, respectively. A lower redox potential shifts the hydrogen evolution reaction backwards (toward water), resulting in a lower hydrogen potential at the Fe/Pd surface, which then reduce the hydrodechlorination activity and the rate of dechlorination by the catalyst. The concentration dependence becomes more remarkable in a solution with higher methanol content because the dechlorination rate is slower, as at a lower temperature. The increasing difference between the k and k_{obs} values in solutions with a higher methanol concentration deserves further investigation.

4. Conclusions

When a catalyst deactivates and keeps a portion of the reactant adsorbed during a catalytic reaction, short-term experiments can be a more useful tool than long-term experiments to study the reaction kinetics. A short-term experimental method was developed here to allow a careful study of the kinetics of PCB dechlorination by using Fe/Pd under various initial conditions. Because the short-term experiments lasted for a very short period of time, deactivation of the catalyst and the resulting changes in the media had not yet played a significant role on the dechlorination kinetics before the experiments ended. The rate constant values, obtained by using a method that minimizes their variation, carry much smaller uncertainty and are more sensitive to the initial conditions. The rate constant values, which do not include the rate of adsorption, represent the actual rate of dechlorination.

The dechlorination results in the short-term experiments indicated (1) that 2-CIBP was dechlorinated by Fe/Pd at a rate not significantly different from the rates for 3-CIBP and 4-CIBP; (2) that the apparent activation energy was between 17 kJ mol⁻¹ and 20 kJ mol⁻¹ over a range of temperature between 4 °C and 60 °C; and (3) that the dechlorination rate decreased significantly in solutions that contained a methanol concentration higher than 10%.

Careful study of the kinetics also indicate that the values of the rate constant were weakly sensitive to the initial concentration in the short-term experiments of 2-CIBP dechlorination in a higher methanol mixture and in water at a lower temperature. The concentration dependence is portrayed by using a Langmuir equation based on a catalytic reaction of a single species, following the Langmuir–Hinshelwood mechanism. The weak dependence is likely an effect of adsorption equilibrium on the rate of the overall process, and

such an effect becomes more notable under conditions when the overall process becomes slow.

Apparent deactivation of Fe/Pd and the resulting changes (such as pH) of the media over the extended period of time attribute to the rate constant values observed in the long-term experiments that were smaller than the rate constant values in the short-term experiments. The actual rate of PCB dechlorination by Fe/Pd in the field can also be affected further by other processes, such as chemical and microbial processes that can cause catalyst poisoning [23]. Use of solvents in field remediation can significantly slow down the rate of dechlorination.

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